Strong competition between velocity-changing and phase-/state-changing collisions in H2 spectra perturbed by Ar

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(Dated: March 11, 2015)

A collisional inhomogeneous broadening of the H_2 Q(1) line perturbed by Ar was observed for the first time 25 years ago. Several attempts were made to explain the line broadening from *ab initio* calculations, which however resulted in fundamental discrepancies between the theory and experiment. To resolve this problem we investigate two possible sources of these differences. First, we repeat the *ab initio* calculations of the broadening and shifting speed dependence, using in the scattering calculations a new, highly-accurate *ab initio* H_2-Ar interaction potential. Second, we replace the previous phenomenological models of velocity-changing collisions with a more physical one based on the interaction potential. This allows us to properly reproduce the experimental broadening over a wide range of temperatures and pressures. We show that this abnormal broadening is caused by strong competition between the velocity-changing collisions and speed-dependent shifting, especially at high pressures.

PACS numbers: 33.70.Jg

I. INTRODUCTION

Inhomogeneous collisional broadening of the isotropic (polarized) Raman Q(1) line of the 0-1 band of H_2 perturbed by Ar, originating from a strong speed dependence of the collisional line shift, was first observed by Farrow *et al.* [1]. Further measurements of the broadening and shifting of this line over a wide range of pressures and temperatures were carried out by Berger *et al.* [2] and Chaussard *et al.* [3]. Many attempts were made to describe the characteristics of the shape of this line in both phenomenological [1, 3–5] and *ab initio* ways [6–10]. The phenomenological models fitted to experimental data reproduced correctly the line shift, width, and its asymmetry in a wide pressure and temperature range. However, the *ab initio* descriptions originating from the H_2-Ar interaction, where none of the parameters was fitted to experimental data, underestimated the line broadening significantly [7–9]. Recently, Tran *et al.* [10] has extended the approach of Waldron *et al.* [9] using a bi-parametric Keilson-Storer model to handle the velocity-changing collisions. Despite the fact that the parameters of the bi-parametric Keilson-Storer model were determined from reliable *ab initio* classical molecular dynamics simulations (CMDS), the effective line width at high densities reported in [10] was still considerably smaller than the experimental width.

In this article we propose an approach for calculating spectral line shapes based on the *ab initio* interaction potential. Using this methodology we obtain agreement between the theoretical and experimental total width of the H_2 fundamental Q(1) line perturbed by Ar, hence resolving a problem that has remained unexplained for 25 years. We treated the phase-/state-changing collisions in a fully *ab initio* way by solving the close-coupling equations for the quantum scattering problem [11–13]. The obtained line broadening and in particular its shifting exhibit strong dependence on the absorber (H_2) speed. In contrast to the previous studies [1, 3–5, 10] the velocity-changing collisions are not described in a phenomenological way, but introduced by means of the *ab initio* interaction potential [14, 15]. Following Refs. [16, 17], we demonstrate that even the use of the simplest hard-sphere approximation of the *ab initio* potential in the speed-dependent billiard-ball profile (SDBBP) [18] leads to a correct reproduction of the experimental spectra.

Proper *ab initio* calculations of molecular spectral line shapes are crucial for diminishing the systematic errors in ultra-accurate Doppler-limited molecular spectroscopy. We show that the use of the appropriate line-shape model allows errors in the validation of quantum-chemical calculations of potential-energy surfaces (PESs) to be eliminated. On the other hand, the use of advanced line-shape models is necessary in order to increase the accuracy in the determination of line positions and intensities. Such accurate measurements are used for testing the relativistic and quantum electrodynamics theories in molecular systems, particularly for H_2 [19–21], which is an excellent playground for such purposes. In the ultra-accurate measurements of line positions the collision-induced shift is measured as a function of pressure and extrapolated to the zero pressure [19–21]. However at room temperature the Doppler width of H_2 lines is of the order of 0.1 cm^{-1} [19–21], while recently achieved accuracy of the determination of the H_2 (3-0) S(3) line position is 5×10^{-5} cm^{-1} [21]. Therefore at this level of accuracy it

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is crucial to properly describe the competition between the speed-dependent shifting and velocity-changing collisions, which is responsible for the formation of the asymmetric line shape and final determination of the line position. The improvement of the transition frequency determination by the use of more advanced line-shape model including the speed-dependent collisional shift was clearly demonstrated by Sinclair *et al.* [22]. The authors were able to reduce the discrepancies between the experimental results and Wolniewicz [23] *ab initio* calculations by more than one order of magnitude comparing to earlier results [24]. The ultra-accurate metrology of H_2 has been already used in a search for exotic physics beyond the Standard Model [25].

Clearly H_2 lines perturbed by Ar are of particular interest from the point of view of spectral line-shape theory. It is so because in this system the differences between real line shape and the ordinary Voigt profile are especially exaggerated. The minimum of the total line width as a function of pressure caused by Dicke narrowing is very pronounced. High perturber/absorber mass ratio makes the velocity-changing collisions very different from the soft collision limit [26]. Moreover the collisional broadening and shifting depend very strongly on the absorber speed. Large spread of collisional shifts for different classes of absorber speed leads to inhomogeneous broadening of the line as well as its asymmetry. All this makes the H_2-Ar system very demanding for testing line-shape models and easily reveals any imperfections of the used treatment. Therefore, the line profile successfully applied in this case should work even better for other systems important for metrological applications and atmospheric research helping to reduce the systematic errors. Spectral line-shape studies play an important role in the spectroscopic determination of the Boltzmann constant and Doppler-width thermometry [27, 28]. Finally, the determination of atmospheric green-house gas concentrations at the sub-percent level, necessary for reliable monitoring of climate change, also requires a more rigorous approach to line-shape modeling [29].

We show that, for the H_2-Ar system, the broadening is significantly influenced by the competition between phase-/state-changing and velocity-changing collisions, which is strong and untypical. This effect can be properly handled only when both the phase-/state- and velocity-/speed-changing collisions are described correctly, especially at high pressures, well above the Dicke minimum. It should be emphasized that for H_2-Ar the inhomogeneous broadening caused by the speed dependence of collisional shifting is much larger than the ordinary collisional broadening. However this inhomogeneous component is significantly reduced by frequent speed-changing collisions. Hence, we have two large effects (the inhomogeneous collisional broadening and the speed-changing collisions), which almost cancel each other. Consequently, even small imperfections in the description of any of them can result in a large error in the estimation of the total line width.

The previously used phenomenological methods of retrieving the pressure broadening parameter γ [2, 3] from experimental spectra were strongly affected by an improper model of the velocity-changing collisions. Hence, the comparison of the experimental pressure broadening coefficient γ with the *ab initio* close-coupling calculations resulted in huge discrepancies [9, 10]. Finally, in contrast to the earlier studies [7–10], we show that the imperfections of previously used PES [30] were not responsible for such a huge underestimation of γ.

II. THE MODEL OF THE LINE SHAPE

A line shape can be calculated via an integral over the active molecule velocity $\vec{\mathrm{v}}$

$$I(\omega) = \frac{1}{\pi}\mathrm{Re}\int d^3\vec{\mathrm{v}} f_m(\vec{\mathrm{v}}) h(\omega, \vec{\mathrm{v}}), \tag{1}$$

where $f_m(\vec{\mathrm{v}})$ is the Maxwellian velocity distribution and where the function $h(\omega, \vec{\mathrm{v}})$ is a solution of the transport/relaxation equation [31, 32]

$$1 = \left\{\Gamma(\mathrm{v}) - i\left[(\omega-\omega_0) - \vec{k}\cdot\vec{\mathrm{v}} - \Delta(\mathrm{v})\right] - \hat{S}^f_{VC}\right\} h(\omega, \vec{\mathrm{v}}), \tag{2}$$

where $(\omega-\omega_0)$ is the light detuning, $\vec{k}\cdot\vec{\mathrm{v}}$ is the Doppler shift, $\hat{S}^f_{VC}$ is the collision operator describing molecule velocity changes, $\Gamma(\mathrm{v})$ and $\Delta(\mathrm{v})$ are the speed-dependent pressure broadening and shifting [33, 34], respectively. The physical interpretation of $h(\omega, \vec{\mathrm{v}})$ is that the product $f_m(\vec{\mathrm{v}})h(\omega, \vec{\mathrm{v}})$ is proportional to the velocity distribution of an optical coherence. We solve Eq. (2) by decomposing the operator and functions in Burnett's basis [18, 31, 35]. This allows the integral equation Eq. (2) to be converted into a set of algebraic equations [32].

Equation (2) implies that the phase-/state- and velocity-changing collisions are not correlated. As was pointed out in Ref. [10] this assumption is justified by the fact that the rate of the velocity-changing collisions is more than two orders of magnitude greater than the rate of phase/state changes.

III. PHASE-/STATE-CHANGING COLLISIONS

First, to describe the phase-/state-changing collisions we have performed close-coupling calculations with the MOLSCAT scattering code [11]. The vibrational motion of H_2 is taken into account while Ar is considered as a structureless particle. We have used Ben Reuven's formalism [12, 13] to obtain, from the scattering S-matrix, the generalized spectroscopic cross sections for line broadening and shifting. Next, the coefficients of the speed-dependent broadening $\gamma(\mathrm{v}) = \Gamma(\mathrm{v})/n$ and shifting $\delta(\mathrm{v}) = \Delta(\mathrm{v})/n$ are calculated as thermal averages of the real and imaginary parts of these cross sections over the perturber velocity [36, 37], where n is the molecular

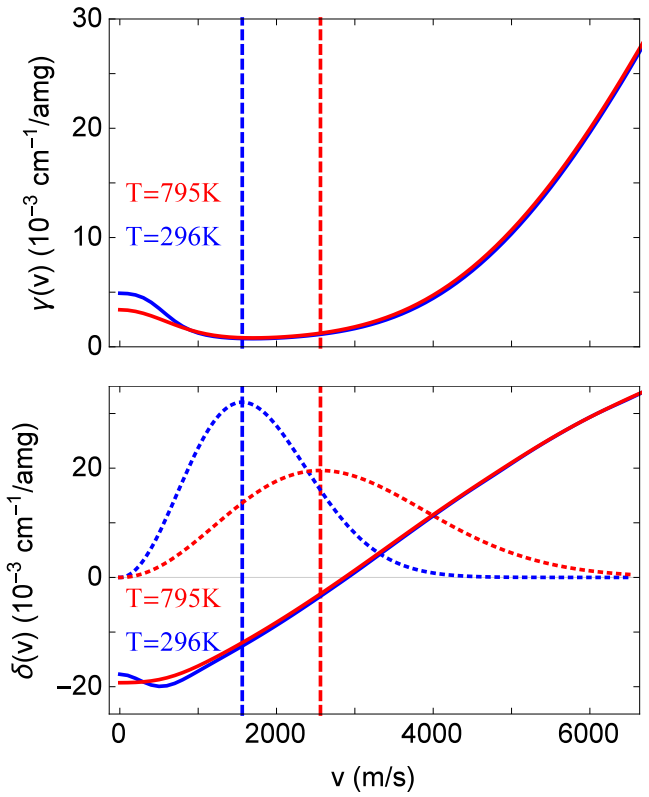

FIG. 1. (Color online) Speed-dependent broadening γ(v) and shifting δ(v) versus the speed of the active molecule for the isotropic Raman Q(1) line of the 0-1 band of H_2 perturbed by Ar. The blue and red lines correspond to $T = 296$ K and $T = 795$ K, respectively. The vertical dashed lines indicate the most probable speeds at these two temperatures. The blue and red dotted lines represent the Maxwellian speed distribution for $T = 296$ K and $T = 795$ K, respectively.

number density, see Fig. 1. The pressure broadening and shifting coefficients, for a given temperature, are defined as $\gamma = \langle\gamma(\mathrm{v})\rangle$ and $\delta = \langle\delta(\mathrm{v})\rangle$, where $\langle\ldots\rangle$ is an average over a Maxwellian velocity distribution. The quantum scattering calculations were performed on our new, highly accurate, PES calculated using the spin-restricted coupled-cluster singles and doubles including noniterative triple excitations [CCSD(T)] method with the large aug-cc-pCVQZ basis and the 332211 midbond basis set, taking into account stretching of the H_2 bond [38]. In the *ab initio* calculations all electrons were correlated; the MOLPRO program 2010.1 [39] and 2012.1 [40] versions were employed. We have also repeated the close-coupling calculations using the semi-empirical PES of Bissonnette *et al.* [30]. We find that the use of our new PES [38] leads to only slight corrections in the generalized spectroscopic cross sections for line broadening, which are even less consistent with the broadening retrieved from experimental spectra [2, 3]. For instance, for the collision kinetic energy of 215 cm^{-1} the cross sections for broadening obtained with our new PES [38] and the PES by Bissonnette *et al.* [30] are 0.300 $Å^2$ and 0.323 $Å^2$, respectively. γ corresponding to the room temperature, obtained from these two PESs is about 1.3×10^{-3} cm^{-1}/amg, which is consistent with previously reported *ab initio* calculations [7, 9, 10]. This value, however, is almost two times smaller than those phenomenologically derived from experimental spectra [2, 3].

The first conclusion of this article, in contrast to those reported in Refs. [7, 9, 10], is that the huge discrepancy between theoretically and experimentally determined line broadening is not caused by imperfections of PESs. It is very unlikely that if both *ab initio* [38] and semi-empirical [30] PESs are incorrect then the cross sections, derived from them, would be almost the same.

IV. VELOCITY-CHANGING COLLISIONS

The second effect of the collisions, described by the $\hat{S}^f_{VC}$ operator in Eq. (2), are the changes in the H_2 velocity, in both its amplitude and direction. The velocity-changing collisions have two consequences on molecular spectra. First, the changes in the molecule velocity can reduce the effective Doppler shift and narrow the Gaussian component of the profile. This confinement narrowing is known as the Dicke effect [41]. Second, dominating at higher pressures, the inhomogeneous broadening originating from the speed dependence of the collisional shift is narrowed by speed class exchanges [16]. To understand the source of the huge discrepancies reported in Refs. [7–10], first, it is crucial to realize that this narrowing increases for larger changes in the molecule speed under the collisions. It was shown [16, 17] (by the comparison of the results with those obtained from CMDS) that the changes of the speed are significantly overestimated by the simple phenomenological models such as hard- or soft-collision models [26, 42]. Therefore, when analyzing their experimental data with a hard-collision model, Berger *et al.* [2] introduced an extra parameter to reduce the effective rate of speed changes. However, the value of the fitted pressure broadening coefficient γ was almost twice as large as the theoretical predictions [7, 9, 10]. Chaussard *et al.* [3] analyzed their experimental spectra with a model combining both hard and soft collisions [43–45]. The soft-collision model was incorporated in an approximated way [46], which neglected collisionally induced speed-class exchanges in relation to phase-/state-changing collisions, see also discussion in Refs. [18, 47]. However, the authors of Ref. [3] obtained almost the same value for the pressure broadening coefficient γ as in Ref. [2]. Recently Tran *et al.* [10] has made an attempt to resolve this problem by applying the more advanced phenomenological biparametric 3D Keilson-Storer model, in which the memory parameters were adjusted to reproduce not only velocity but also speed autocorrelation functions deduced from CMDS [48]. Despite the qualitative improvement of the velocity-changing model, this approach resulted in only a slightly better agreement with measurements;

at high pressures and room temperature, the experimental line width was still about 40% larger than the model prediction.

In this study, we replace the phenomenological description of velocity-changing collisions with a more physical approach based on the quantum mechanical *ab initio* PES. We represent the H_2-Ar interaction by the hard-sphere potential adjusted such that the hard-sphere wall intersects the isotropic component of the PES at the mean collision energy $\epsilon = k_B T$, where T is the temperature and k_B is the Boltzmann constant. Note that the potential-well depth is much smaller than ϵ. The hard-sphere approximation for H_2-Ar was verified by comparing hard-sphere collision kernels and relaxation times with those obtained from CMDS [17].

V. RESULTS

To validate our model we directly compared the total half width at half maximum (HWHM) and the shift of our calculated SDBBP [18] with the experimental values by Berger *et al.* [2] and Chaussard *et al.* [3], see Fig. 2. The experimental data [2, 3] was collected for a mixture of 95% of Ar and 5% of H_2, taken into account in our calculations by considering the collision operator as a weighed sum of H_2-H_2 and H_2-Ar collision operators [17]. The speed-dependent broadening and shifting associated with the H_2-H_2 collisions were taken from Ref. [49, 50] (see also Appendix C in Ref. [17]). The upper panel in Fig. 2 illustrates that our calculated values of the HWHM of SDBBP agree with the measurements to within experimental noise at both 296 K and 795 K. It should be noted that our calculations originate only from an *ab initio* PES and no parameter was adjusted or fitted to experimental data. Note also that the speed-dependent broadening and shifting associated with the H_2-H_2 collisions taken from Ref. [49, 50] were determined from the fit to experimental data; however, this has a small impact on our results since the concentration of H_2 is only 5% and the speed dependence of collisional shift is about 2.5 times weaker for the H_2-H_2 collisions than for the H_2-Ar ones (compare the slopes of the δ(v) curves from Fig. 1 and from Eq. (C4) given in [17] with parameters taken from [49]). Moreover, for H_2-H_2 the competition between the collisional speed changes and speed-dependent shifting is less sensitive to the form of the speed-changing model due to a smaller absorber to perturber mass ratio [51], which is equal to one in this case.

To show the importance of a proper description of speed-changing collisions we also simulated the line width and shift for soft- and hard-collision models (the soft collisions were incorporated in an exact manner as a limiting case of SDBBP [18] where the perturber to absorber mass ratio approaches zero) - see dashed and dotted lines in Fig. 2. The line width predicted by these models is much smaller than the experimental one, which has already been demonstrated in Ref. [16, 52]. As mentioned earlier, this is a consequence of greatly overestimated speed changes by these models [17]. On the other hand, the line shift is almost independent of the model of the velocity-changing collisions (note the overlap of the solid, dashed and dotted lines in the lower panel in Fig. 2). Possible sources of discrepancies between simulated and experimental shifts are PES imperfections and neglecting the correlations between phase-/state- and velocity-changing collisions [53, 54]. The line shifts determined from the close-coupling calculations with our new PES [38] are close to those determined in Ref. [10] with the PES of Bissonnette *et al.* [30], which are in good agreement with the experimental results (see Fig. 3 in Ref. [10]), in contrast to the collisional widths, which are very dependent on the model used to derive them from experimental line shapes. However, intrinsically for this system, at $T = 795$ K it is difficult to calculate the line shift with high accuracy, because even small differences in the speed-dependent shift-

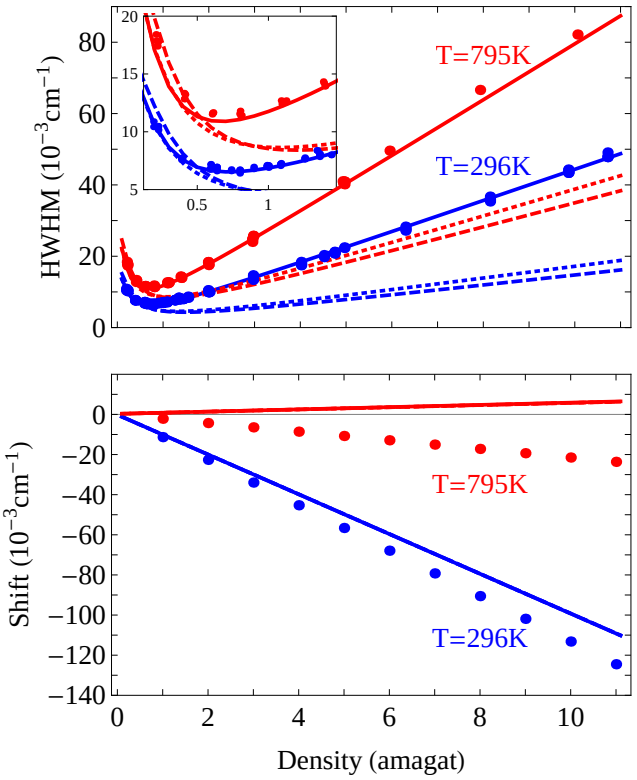

FIG. 2. (Color online) The total half width at half maximum (HWHM) and the shift (center of gravity) of the spectral line shape as a function of number density for the isotropic Raman Q(1) transition of the 0-1 band of H_2 perturbed by Ar. The solid lines represent the results of our calculations using SDBBP [18], while the points correspond to the experimental values [2, 3]. The dashed and dotted lines represent our theoretical calculations in which the velocity-changing collisions model was replaced with phenomenological soft- and hard-collision models, respectively. The concentration of Ar was 95% (in the experiment as well as in our calculations).

ing $\delta(v)$ (see lower panel in Fig. 1) lead to large relative differences in the effective line shift (see lower panel in Fig. 2). The reason for this is the fact that $\delta(v)$ is almost centered around zero and the value of the effective line shift is much smaller than the range of $\delta(v)$ values. This observation is also consistent with experimental results obtained by Chaussard *et al.* [3] showing that the sign of the line shift changes at high temperature.

VI. CONCLUSIONS

To sum up, in this work we have shown that the SDBBP [18] calculations based on an intermolecular interaction potential [17] explains the physical mechanism responsible for the anomalously high broadening of H_2 transition observed in experiment [3], which was significantly underestimated by previous theoretical studies [7–10]. Moreover our results contradict the conclusions reported in Refs. [7–10], where it was stated that the fundamental discrepancy between theory and experiment originates from some defects in the PESs used to calculate phase-/state-changing collisions. We have demonstrated that the key factor needed to explain the experimental line broadening is a proper description of the velocity-changing collision. In our approach we have replaced the phenomenological models used previously (which overestimate the rate of the speed changes) with a more physical one based on the interaction potential, i.e. we approximated the PES with the hard-sphere potential, which has already been shown to properly reproduce the velocity-changing collisions for H_2-Ar and H_2-H_2 [17]. These results are important not only for understanding the principal physical mechanisms lying behind the formation of inhomogeneously broadened spectra, but also for recently rapidly developing ultra-precise optical metrology based on Doppler-limited molecular spectroscopy, where a proper modeling of molecular spectra is necessary to avoid additional systematic errors in fundamental studies [19–21, 25, 27, 28].

ACKNOWLEDGMENTS

The authors are grateful to F. Chaussard for discussion and providing the experimental data. P.W. is supported by the National Science Centre, Poland, Project No. DEC-2013/09/N/ST4/00327. The research is a part of the program of the National Laboratory FAMO in Toruń, Poland. The research is partially supported by the Foundation for Polish Science TEAM Project co-financed by the EU European Regional Development Fund. The financial support provided by the PHC POLONIUM program is acknowledged. The authors acknowledge the computational grant G51-15 from the Interdisciplinary Centre of Mathematical and Computer Modelling (ICM) of the University of Warsaw. The use of resources of Wrocław Center for Networking and Supercomputing (WCSS) is also gratefully acknowledged.

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